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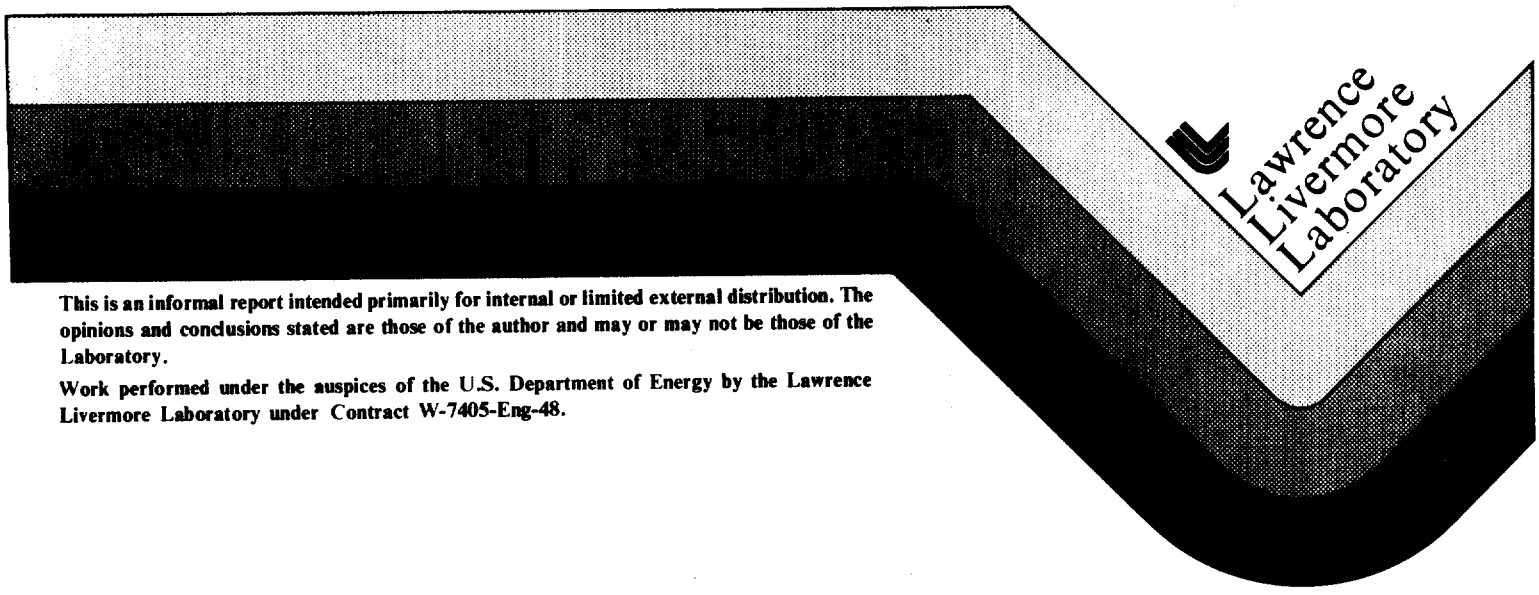
February 1981



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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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The Analysis of Composites Containing Ethylenediamine Dinitrate, Ammonium Nitrate, and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

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ABSTRACT

Methods are presented for the analyses of composites containing ethylenediamine dinitrate (EDD), ammonium nitrate (AN), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Two composites also contained aluminum powder. The procedures are sequential extraction methods for aluminum and RDX and a novel volumetric method for EDD involving titration with standard Cu(II) solution. This method may be specific for vic-diamines and their salts.

INTRODUCTION

Work is in progress at this Laboratory on the detonation calorimetry of composites containing ethylenediamine dinitrate (EDD), ammonium nitrate (AN), and RDX. Some composites contained, in addition, aluminum powder or potassium nitrate. The nominal compositions are listed in Table 1. Assay methods for these composites were required and are described in this report. They involve a combination of extraction-gravimetric and volumetric procedures.

EXPERIMENTAL

1. Analysis of EAR (EDD/AN/RDX)

1.a. Extraction-gravimetric analysis of RDX

Approximately 5 g of the composite was accurately weighed into a beaker. Fifty to 100 ml of distilled water was added and the mixture was brought to boiling on a hot plate. The

Table 1. Nominal compositions of various composites

Component	EAR %	EARL-1 %	EARL-2 %	EARK %
EDD	42.5	40.3	36.2	42.4
AN	42.5	40.3	36.2	36.1
RDX	15	14.2	12.8	15
Al	-	5.2	14.8	-
KNO_3	-	-	-	6.4

solution was then allowed to cool to room temperature and quantitatively filtered through a medium-porosity filter crucible into a 500-ml volumetric flask. Beaker and crucible were washed with additional portions of distilled water which were combined with the filtrate in the volumetric flask. The beaker and crucible were dried in a vacuum oven at room temperature to constant weight. The residue consists of RDX; the loss in weight equals the amount of EDD plus AN. The volumetric flask was diluted to volume with distilled water and used for the determination of EDD and AN. (See 1.c. and 1.d.)

1.b. Standardization of approx. 0.02 N Cu(II) solution.

The titrant for EDD was approximately 0.02 N cupric sulfate (0.01 M) prepared by dissolving 2.5 g of the pentahydrate in 1 liter of distilled water. A stock solution of the input EDD was prepared, containing approx. 9-10 mg of EDD per 10 ml. Ten ml aliquots of this solution were accurately pipetted into a 50-ml beaker containing a stirring bar. The solution was diluted to 25 ml with distilled water and the pH adjusted to 9.0 $\pm$ 0.1 with dilute ammonium hydroxide using a pH meter. The titration system in the present work was controlled by a Tektronix 4051 graphics system previously described[1]; however, any suitable titration equipment may be

used. Emf's were monitored with a solid-state cupric ion-selective electrode and a single-junction reference electrode. Stirring was provided by a magnetic stirrer. The stirring motor was separated from the titration vessel by a water-cooled plate for thermal isolation and by an aluminum plate connected to ground to reduce electrical noise. Titration endpoints were calculated as previously described.[1]

1.c. Analysis of EDD.

Suitable aliquots of the filtrate from Step 1.a. were accurately pipetted from the 500-ml volumetric flask containing the aqueous extract of the composite. They were treated in the same way as the EDD standard solution and titrated potentiometrically with the standard cupric solution.

1.d. Analysis of AN.

EDD plus AN can be determined by the formol titration which has been reported previously.[2] However, for most purposes, AN may be calculated by difference from the result of the determination of EDD.

2. Analysis of EARL-1 and EARL-2.

2.a. Extraction-gravimetric analysis of RDX and aluminum.

The aqueous extraction procedure is the same as 1.a. (page 1); however, the residue consists of RDX plus aluminum. This residue is then subjected to a second extraction, with acetone. Sufficient acetone should be used to insure complete removal of the RDX. Beaker and crucible are again dried in vacuo at room temperature to constant weight. The residue is aluminum only. The amount of RDX is calculated from the difference in weights between the first and second extraction.

2.b. Analysis of EDD and AN.

The procedures are the same as those previously presented under 1.b through 1.d.

RESULTS AND DISCUSSION

We have previously reported an analytical method for a eutectic mixture of EDD and AN.[2] Both components were determined by potentiometric titration with standard sodium hydroxide after reaction with formaldehyde. EDD exhibited 2 breaks in the titration, while AN exhibited only a single break. The first break was a measure of the EDD content, while the second break was a measure of the sum of the components.

We have now discovered a selective titrimetric method for EDD, which may be applicable to other vic-diamines and their salts. In this titration 2 mol of EDD react with 1 mol of Cu(II). As the titration progresses, the solution turns a distinct violet/purple color, quite different from the color of the cupric ammonia complex. We have found that the optimum pH for this titration is between 9 and 9.5 (which is adjusted using dilute ammonium hydroxide), but the titration is feasible between pH 8.2 and 9.7. Under the same conditions AN is not affected.

Copper forms a chelate-ring complex with ethylenediamine.[3] The additional stability given to metal complexes by chelate ring formation is well known. Thus, for $Cu(NH_3)_4^{2+}$ the overall stability constant is $10^{12.6}$ while for ethylenediamine-Cu(II) it is $10^{20.0}$; in other words, the stability constant for the ethylenediamine complex is approximately 10 million times greater.[3] The ethylenediamine-Cu(II) complex has a maximum absorption near 550 nm; we have, however, made no attempt to perform a spectrophotometric determination. Copper complexes of other diamines have also been reported. A complex with propylenediamine was reported by Hall and Carpenter[4], and those with diethylenetriamine and ethylendiamine by Kuba and Banic.[5]

A typical titration curve for 9.6 mg of EDD vs 0.02 N Cu(II) is presented in Figure 1. This method is more specific than the previously used formol titration.[2] In addition, no blank determination is necessary.

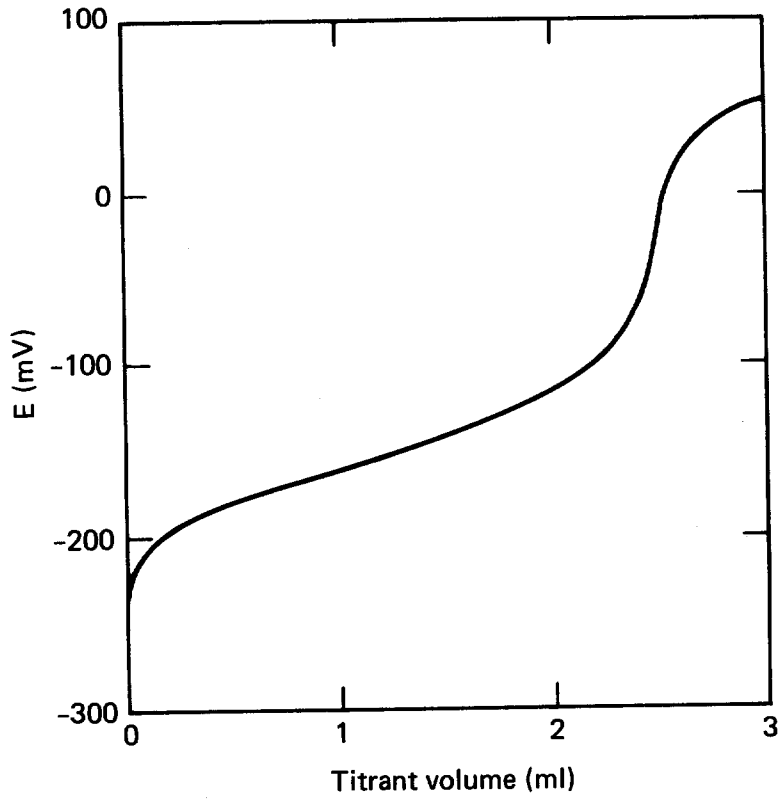

Figure 1. Titration of 9.6 mg of EDD vs. 0.02 N Cu(II) at pH 9.0

Results for EAR, EARL-1, and EARL-2 are given in Table 2. The results are based on a single 5 g sample. Only one value is available for RDX and aluminum. The standard deviations for EDD and AN are based on repetitive aliquots of the aqueous filtrate solution. Preliminary results on smaller samples (20 mg) showed considerable variation; we decided to use a fairly large sample to eliminate errors resulting from non-homogeneity.

We have also reanalyzed a previously reported sample of AN and EDD only.[2] The results were 51.12% EDD with a standard deviation of 0.12% for 6 replicates. The results for the formol titration were 51.23% EDD.

Table 2. Analysis of various composites

Component	EAR %	EARL-1 %	EARL-2 %
EDD	43.04 (0.06)[a]	41.12 (0.16)	36.52 (0.11)
AN	41.35 (0.05)	40.86 (0.16)	35.59 (0.11)
RDX	15.60	11.86	12.73
Al	-	6.16	15.16

[a]standard deviations given in parentheses

We have not analyzed the sample of EARK (EDD, AN, RDX, and KNO_3) because of budgetary constraints. We suggest, however, the following scheme for possible analysis of this composite:

1. Aqueous extraction of the soluble components (AN, EDD, and KNO_3) and gravimetric determination of RDX.
2. Titration of EDD in the aqueous extract as for the other composites (see 1.c.).

3. Determination of EDD and AN by the formol titration, and calculation of KNO_3 by difference.

4. KNO_3 may also be titrated with 0.1 N sodium tetraphenylborate using a fluoroborate indicating electrode and a double-junction reference electrode (with a salt bridge of sodium nitrate).

In this titration ammonium ion must be complexed by the addition of formaldehyde and adjusting the pH of the solution to 7 with sodium hydroxide.

ACKNOWLEDGEMENT

The writer wishes to thank Glendon L. Crossman for the extraction-gravimetric analyses of RDX and aluminum.

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